Bulgarian Chemical Communications, Volume 45, Number 4 (pp. 635–643) 2013

Surface and photocatalytic properties of nanostructured ZnO thin films doped with iron

N. Kaneva[1], A. Ponomareva[2], L. Krasteva[1], D. Dimitrov[1], A. Bojinova[1]*, K. Papazova[1],
G. Suchaneck[2], V. Moshnikov[3, 4]

[1] *Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry,*
Faculty of Chemistry and Pharmacy, University of Sofia, Sofia 1164, Bulgaria
[2] *Solid State Electronics Laboratory, TU Dresden, Dresden 01062, Germany*
[3] *Micro- and Nanoelectronics Department, Saint-Petersburg State Electrotechnical University (LETI),*
Saint-Petersburg 197376, Russia
[4] *Department of Integrated Electronics, Saint-Petersburg State Polytechnical University,*
Saint-Petersburg 195251, Russia

Received February, 2013; Revised May, 2013

In this work, we investigate nanosized Fe-ZnO thin films, deposited on glass substrates by sol-gel method and dip-coating technique. The precursor sol is prepared by dissolving of $Zn(CH_3COO)_2.2H_2O$ and $Fe(NO_3)_3.9H_2O$ in 2-methoxyethanol with addition of monoethanolamine as surfactant. The Fe content in the ZnO thin films is selected to be 0.25, 0.5 and 1 wt.%. Thin nanostructured films with two different coatings structures are prepared for the photocatalytic tests. The first one is formed by deposition of Fe-doped layer by 5 dip-coating cycles on standard microscopic glass slides. The second type of hierarchically structured films is deposited onto glass substrates by two – step procedure. The photocatalytic efficiency of the prepared films is tested using a textile dye, Reactive Black 5 (RB5) in aqueous solutions at different initial dye concentration, under UV or visible light irradiation. The dependence of photocatalytic activity on the (i) Fe content, (ii) presence or absence of ZnO sublayer under Fe doped layer, (iii) frequency of irradiation and (iv) initial concentration of dye are investigated. For explanation of the observed results a comprehensive AFM investigation including fractal analysis of surface topography is performed. The relationship between the observed photocatalytic behavior of the film samples and the obtained by AFM surface features is discussed.

Key words: ZnO:Fe thin films, sol gel, photocatalysis, Reactive Black 5, UV and visible light.

INTRODUCTION

In the last decades, a large number of research groups worldwide focused their attention on investigations on the use of sunlight, (5–7% UV, 46% visible and 47% infrared radiation) as a beneficial natural energy source for photocatalytic applications [1, 2]. Nowadays, there is a large problem in water purification from harmful pollutants (such as dyes, drugs, hormones, heavy metals traces) in low concentrations. The most widely used photocatalyst TiO_2, has a relatively large band gap (for anatase modification E_g=3.2 eV) and is low a cost, natural, chemically stable and nontoxic material [3]. Zinc oxide has similar band gap (E_g=3.2 eV) and is favored is favored in comparison to TiO_2, in some applications due to its higher quantum efficiency [4–6]. However, the band gap of the above mentioned semiconductors require near UV irradiation for their photoactivation. Therefore, different methods have been used to achieve an efficient visible light photocatalysis by these oxides, such as doping and co-doping with nonmetals [7–9] and transition metals [10, 11], surface modification [12, 13] and composite materials [14–16]. However, no matter of its unique optical [17–20], magnetic [21, 22], electrical [23] and gas-sensing properties [24–27], only few investigations have reported on the photocatalytic photodegradation of organic contaminants with Fe-doped ZnO [28, 29].

There are a large number of commonly used dyes available at the market. Between them, the most used are reactive azo dyes. Additionally, these dyes are the most problematic pollutants in textile waste-

---

* To whom all correspondence should be sent:
E-mail: nhasb@wmail.chem.uni-sofia.bg

waters. The reason is that after the reactive dyeing process is finished, more than 15% of the textile dyes is lost in wastewaters during dyeing operation [30]. So, in this work, we have selected Reactive Black 5 dye (RB5), one of the most used reactive dyes for textile finishing, as representative azo dye pollutant for contaminated wastewaters from textile manufacturing.

Textile wastewaters are large problem for conventional treatment plants in the entire world. The release of these wastewaters into enviroment is harmful to aquatic life and mutagenic to human beings. The removal of organic pollutants from wastewater by heterogeneous photocatalysis is an important method in environmental protection. As a well-known photocatalyst, much attention has been paid to ability of ZnO in degradation and complete mineralization of dyes and other environmental pollutants.

In this study we present for the first time nanosized hierarchical Fe-ZnO (Fe-content 0.25, 0.5 and 1 wt.%) thin photocatalytic films, deposited on glass substrates via sol-gel method and dip-coating technique. The aim of this research is to investigate and establish the dependence of photocatalytic activity on the: (i) Fe content; (ii) existence or absence of ZnO sublayer under Fe doped layer; (iii) frequency of irradiation and (iv) initial concentration of dye.

EXPERIMENTAL

Materials and reagents

The following materials were used to manufacture ZnO thin films: zinc acetate dehydrate, $Zn(CH_3COO)_2.H_2O$, (≥99.5%), 2-methoxyethanol (≥99.5%), monoethanolamine (≥99.0%) and iron nitrate hydrate, $Fe(NO_3)_3.9H_2O$, (≥99.0%) from Fluka. The glass slides (ca. 76×26 mm) for substrates of ZnO films were from ISO-LAB (Germany). Reactive Black 5 ($C_{26}H_{21}N_5Na_4O_{19}S_6$, λ_{max}=595 nm, dye content ca. 55%) was from Sigma-Aldrich. Distilled water was used in the preparation of dye solutions.

ZnO and ZnO:Fe synthesis

Zinc oxide thin films with different concentrations of Fe^{3+} doping (0.25, 0.5 and 1 wt.%) were deposited on glass substrate by sol–gel method. The precursor sol is obtained using zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine. As starting materials, zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] and iron nitrate hydrate [$Fe(NO_3)_3.9H_2O$] were dissolved in 2-methoxyethanol. Then, sol stabilizer, monoethanolamine (MEA) equimolar to the [Zn^{2+} + Fe^{3+}], was added to the above solution. The substances were mixed together in a round-bottom flask and stirred at room temperature for 15 min. The obtained clear solution was heated up at 60 °C upon magnetic stirring for 60 min and let to age overnight. The resultant solution was clear and homogenous to serve as the coating substance for films. No visible changes were observed in the sol upon standing of the precursor at room temperature for at least 2 months.

Preparation of the coating solution

The dip coating is a simple and cheap technique for deposition of thin oxide films. The deposition of a layer of oxide material can be optimized by controlling precisely the immersion and withdrawal speed, number of dipping cycles and solution viscosity for the purpose of deposition of a layer of oxide material.

The ZnO films were prepared by dip coating, drying and sintering of the material. Glass surfaces (5×5 cm) were coated with the coating solution by means of dip coating apparatus and withdrawing it at rates of 0.9 cm/min at room temperature deposited the gel films. It was found that higher withdrawal rates result in films of lower quality. The films were dried for 15 min at 80 °C in air after each successive coating. The as-prepared gel films were annealed at 500 °C for 60 min in order to obtain the final ZnO films.

Thin nanostructured films with two different coatings configurations were prepared for the photocatalytic tests. The first one was formed by deposition of the Fe doped layer by 5 dip-coating cycles onto standard microscopic glass slides. For producing of the second configuration, the glass slides are covered firstly with a pure ZnO layer formed by 2 dip-coatings, prior the deposition of doped with Fe ZnO layer produced by 3 dip-coating cycles. The final iron doped films had slight orange-brownish coloration, typical for the formation of Fe_2O_3, as expected at the particular experimental conditions, applied for films preparation.

Characterization of the films

The as-obtained at different annealing temperatures ZnO thin films were analyzed by scanning electron microscope (SEM) JSM-5510 (JEOL), operated at 10 kV of acceleration voltage. Before imaging, the investigated samples were coated with gold by JFC-1200 fine coater (JEOL). The surface morphology of ZnO films (pure and doped with iron) was additionally examined by atomic force microscopy (AFM) using an INTEGRA Therma scanning probe microscope (NT-MDT, Zelenograd, Russia). Tapping mode imaging was performed in air using silicon cantilevers (Type NSG01, NDT-MDT, Zelenograd, Russia). In this work, fractal dimension analysis was performed by means of the Open Source Software Gwyddion 2.21 [31] using two different approaches: the cube counting method and the triangulation method [32]. The crystalline phase identification and unit cell parameters evaluation was performed by X-Ray diffraction analysis using Siemens D 500 diffractometer (CuKα source of radiation at a step of 0.05 deg for 2Θ and counting time 2s/step).

Photocatalytic degradation tests

The photocatalytic performance of the films was examined using the degradation of Reactive Black 5 dye in aqueous solution. Nanostructured films with two different configurations of the coating structures were studied and compared for decolorization of textile dye (initial concentration was 3, 5 or 10 ppm).

The measurement was conducted in cylindrical glass vessel of 150 ml volume, equipped with a magnetic stirrer and UV-lamp above (maximum emission at 370 nm). The light power density at the sample position was 0.66 mW/cm^2. The light irradiation was measured with research radiometer of Ealing Electro-optics, Inc. The lamp was fixed at ~15cm above the treated solution. The decolorization process of RB5 was monitored by UV-Vis absorbance spectroscopy after aliquot sampling at regular time intervals. Each aliquot sample was returned back to the reaction vessel immediately after the spectrophotometrical measurement. All photocatalytic tests were performed at a constant stirring rate (500 rpm) and room temperature (23±2 °C). The effect of initial concentration of RB5 (3, 5 and 10 ppm) on the photocatalytic performance of the films was also investigated. In all experiments the optical absorbance spectra were measured by spectrophotometer Jenway 6400 in the wavelength range from 400 to 800 nm. Control experiments without any illumination (the reaction system was kept in darkness) were also performed. The decolorization rate of RB5 is followed with time spectrophotometrically at a wavelength of 595 nm (the wavelength of maximum absorbance).

The degradation degree of Reactive Black 5 (%) was calculated as:

$$D\% = \frac{C_0 - Ci}{C_0} x100 \qquad (1)$$

Here C_0 is the initial concentration of dye and C_i is the concentration of the dye after irradiation at selected time interval t_i.

To investigate the photoinstability of pure and doped ZnO films, produced in the current work, some of the photocatalytic experiments were repeated three times, using a new dye solution with the same initial concentration in each measurement. All the results were reproducible. The absence of photocorrosion was also checked by Scanning Electron Microscopy after finishing of all the three photocatalytic experiments of the samples. No changes of the ganglia-like hills and wrinkled morphology of the films was observed, which make us to conclude that this kind of structure may increase somehow photostability of the films and this is the subject of our future investigations.

RESULTS AND DISCUSSION

Structure characterization

Recent review [33] summarizes the main chemical routes used in the sol–gel synthesis of ZnO thin coatings and highlights the chemical and physical parameters (precursors nature and concentration, type of additive, coatings method, pre- and post-heat treatment) influencing films structural properties. SEM images of the films, prepared by first method were investigated in order to show how their surface morphology influences the photocatalytic properties (Fig. 1). The morphology is homogenous with the ganglia-like hills of a width 0.5–1 μm, length ~5 μm and height about 1μm (Fig. 1a). The Fe-doped ZnO films express similar morphology, as seen from the surface micrographs of samples with 0.25–1 wt.% Fe^{3+} (Fig. 1b and 1c). In the case of Fe-containing films, the ganglia are of a typical width 0.1–0.5 μm, length from 1 μm to 5 μm and height of about 2.5–3 μm. The increase of Fe^{3+} content leads to decrease of the volume and size of ganglia-like hills, which look more distorted and branched at their ends. The ganglia-like hills are smaller and the morphology is not homogenous.

Fig. 2 shows the AFM-images of the samples recorded in tapping mode. It is well known that AFM provides already a digitized image suitable for numerical evaluation. Surface texture is characterized by the height of its peaks, the depths of its valleys and the distances that separate them. Surface topography is usually described in terms of surface roughness. Sometimes the root mean square roughness (RMS) is associated to grain size of film. However, surface roughness is solely a function of height, that is, information about lateral topography is lost. The calculation of the fractal dimension gives a more general description than the RMS surface roughness alone.

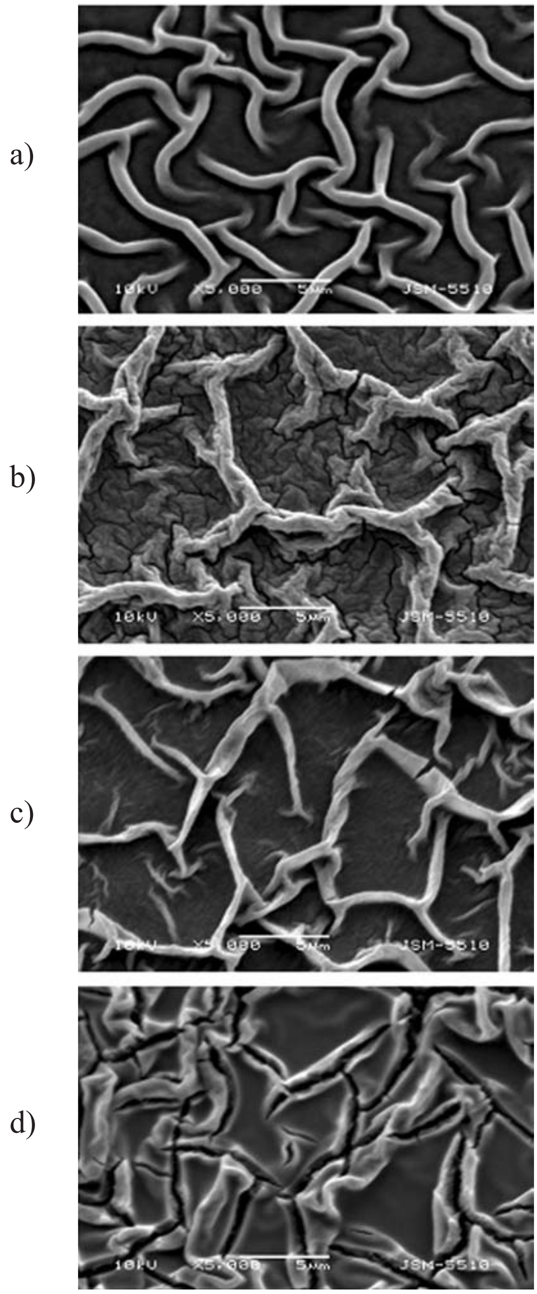

Fig. 1. SEM images of ZnO films prepared by first method at different concentrations of Fe^{3+} doping: (a) 0%; (b) 0.25%; (c) 0.5% and (d) 1%

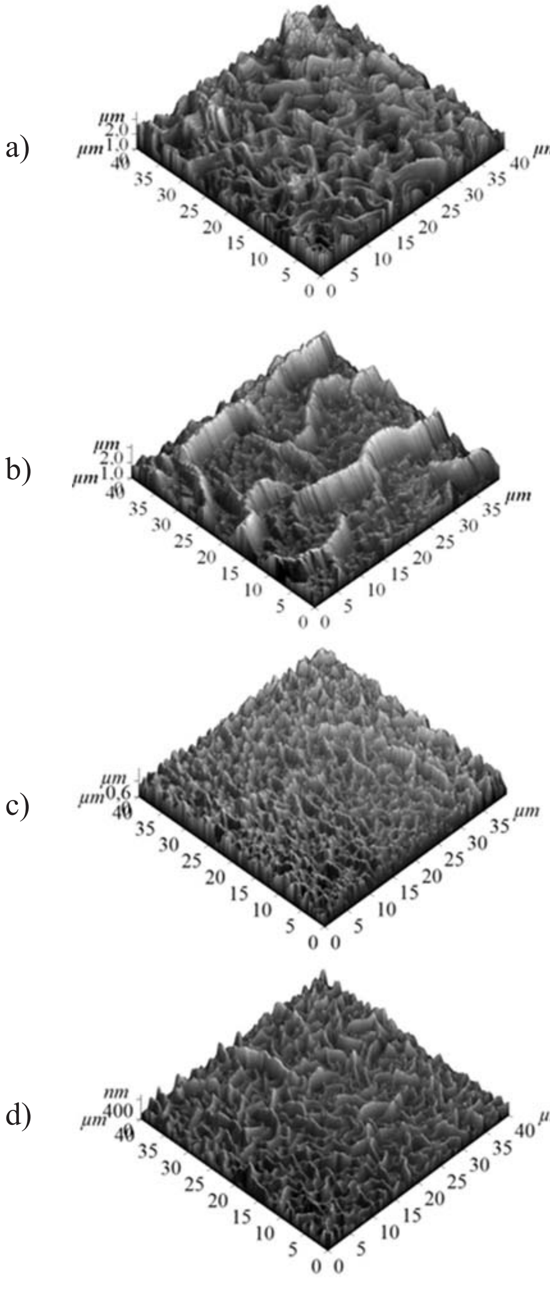

Fig. 2. AFM images of ZnO doped with Fe^{3+}: (a) 0%, (b) 0.25 wt%, (c) 0.5 wt% and (d) 1 wt%

A fractal is a set for which the so called fractal dimension D_f always exceeds the topological dimension, but it is smaller than Euclidian dimension of the space where the fractal is embedded. Fractal dimension of a line in two-dimensional space characterizes the ratio of the change in detail to the change in scale of a fractal pattern [32].

$$D_f = \lim_{\varepsilon \to 0} \frac{\lg N}{\lg(1/\varepsilon)} \tag{2}$$

where N is the number of sticks measured using the scaling factor ε. Surfaces in three-dimensional spaces are approximated using scaled cubes or tri-

Table 1. Fractal dimensions and the roughness characteristics of ZnO nanocomposites in dependence on iron doping concentration

Composition	*Ra*, μm	*RMS*, μm	D_f
Pure ZnO	0.412	0.513	2.47
ZnO+0.25 wt% Fe	0.293	0.373	2.43
ZnO+0.5 wt% Fe	0.250	0.306	2.41
ZnO+1 wt% Fe	0.159	0.190	2.37

angles. In case of film growth on a two-dimensional substrate, the fractal dimension lies within the range $2 \leq D_f \leq 3$, where a flat surface has a value $D_f = 2$ and an increasing value of D_f represents an increasing surface roughness [32]. An advantage of AFM images is that they are already digitized as required for numerical evaluation of fractal dimension. Here, the scaling factors range from pixel size to half of the scan length of the image.

Fractal analysis of AFM-images allows detecting surfaces local fractal dimensions. Due to a self-affine surface (self-affinity refers to a fractal whose units are scaled by different amounts in the x- and y-directions), a local fractal dimension appears which characterizes the increase in surface size compared to a smooth surface.

The surface topography plays a crucial role in predicting catalytic properties [32]. Obviously, the larger surface area and roughness provide greater number of activation centers which can fit on it. Therefore the higher value of fractal dimension can indicate higher catalytic activity. Both the cube counting and triangulation methods of fractal analysis [31, 32] gave similar values. All roughness characteristics the arithmetic average roughness (*Ra*), the root mean square roughness (RMS) and the fractal dimension (D_f) are significantly affected by Fe^{3+} fraction. These parameters decrease with the increasing of iron content (Table 1). The decrease of fractal dimension with increasing of Fe^{3+} content is correlated with results of photocatalytic activity investigation, as described below.

The XRD spectrum (Fig. 3) of the clear ZnO thin film consists of well-defined diffraction peaks showing good crystallinity. The (100), (002), (101) diffraction peaks of the sol-gel films appear clearly at the annealing temperature, which can be attributed to the hexagonal wurtzite structure of ZnO. The thin films consist in this case of polycrystalline grains with no preferential growth observed. The calculated by Scherer crystallite size is 30 nm. Nanostructure doped films contains a small amount of iron (0.25, 0.5 and 1 wt.%), which is not captured by the X-ray diffraction.

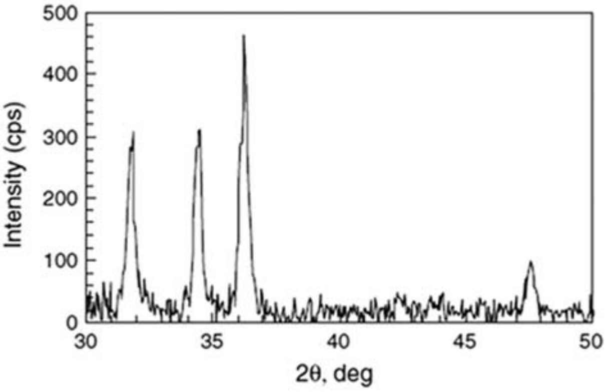

Fig. 3. XRD spectra of clear ZnO films annealed for 1 h at 500 °C.

Photocatalytic activity

In this work we photodegrade the dye Reactive Black 5 (RB5), one of the most used reactive dyes for textile finishing, as a representative dye pollutant for industrial wastewaters. The bleaching rate of RB5 is followed with time spectrophotometrically at a wavelength of 595 nm (the wavelength of maximum absorbance).

The photodegradability of the dye is investigated by exposing the dye solution under UV light in the presence of undoped and doped ZnO photocatalyst, prepared by the two different methods. The dependence of the degradation rate on time under UV-light is illustrated in Fig. 4. The figure compares the kinetic curves of RB5 decolorization of undoped and doped ZnO photocatalyst with the irradiation time. The pure ZnO films have the highest decolorization percentage under UV-light illumination (more than 90% in 180 min of irradiation). The ZnO doped with Fe^{3+} samples (0.25 wt%, obtained by the first method) have higher photocatalytic efficiency and faster mineralization RB5 (D = 68.75%) than those, prepared by the second method (D = 52.25%, Fig. 4). Therefore, we investigated more completely

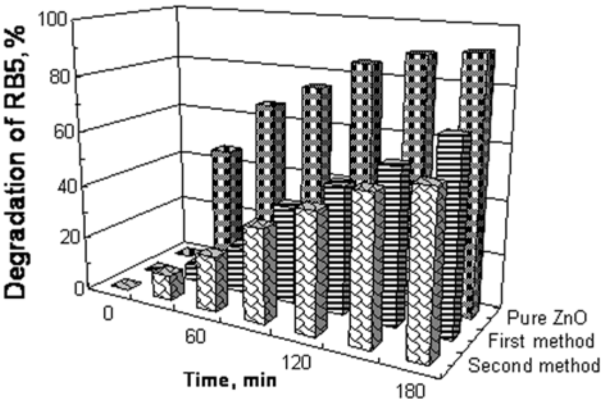

Fig. 4. Photocatalytic degradation of the Reactive Black 5 concentration (3 ppm) in aqueous solutions under UV-light illumination of ZnO and ZnO-Fe (0.25 wt%) films, deposited by two methods

the photocatalytic properties of the films, obtained by the first method.

Fig. 5 shows bleaching kinetics of RB5 in aqueous solutions by ZnO and ZnO:Fe films under UV and visible light illumination. The reaction kinetics is revealed by plotting the natural logarithm of concentration ratio, ln(C/C_0), versus the irradiation time, t. The solid lines indicate that the reaction is of first order kinetics. They are plotted following the equation below:

$$\ln(C/C_0) = -kt \tag{3}$$

where, C_o is the initial absorbance of dye solution, C is the absorbance at time t, and k is the reaction rate constant. The value k is evaluated from the respective logarithmic plots of the experimental data.

As seen from Fig. 5, the pure ZnO film has the highest photocatalytic activity, which corresponds to a highest k value (under UV and visible, $k_1 = 0.0153$ min^{-1} and $k_2 = 0.0095$ min^{-1}). The photocatalytic activity of the doped ZnO is rather low. It is interesting to note that the k values of composite film with ZnO:Fe (under UV and visible, $k_1 = 0.0013$ min^{-1} and $k_2 = 0.0008$ min^{-1}) is considerably lower than that of pure ZnO. These experimental results are obtained for two independent series of experiments – under UV or visible light illumination.

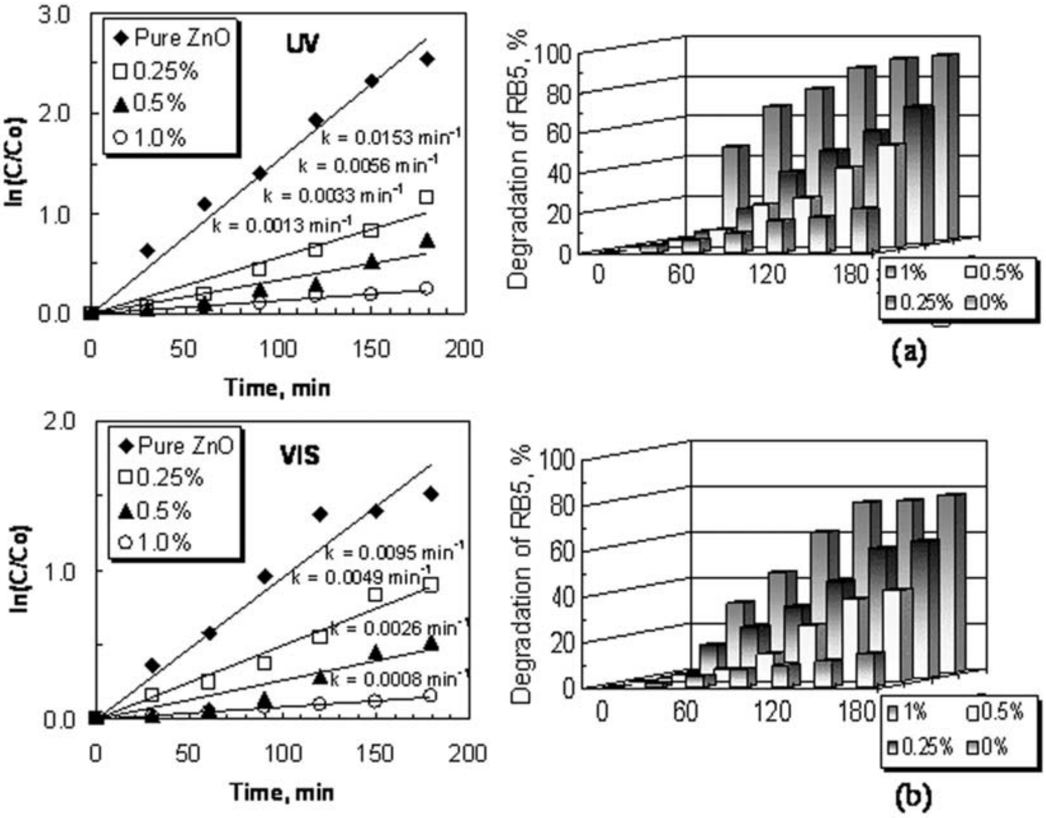

Fig. 5. Bleaching kinetics of RB5 in aqueous solutions by ZnO and ZnO-Fe films under (a) UV and (b) visible light illumination. The initial concentration of dye was 3 ppm

Nanostructured ZnO films degrade faster the dye (under UV and visible, D_1 = 97.76% and D_2 = 78.45%) and have the better photocatalytic properties compared to ZnO films doped with 1 wt.% iron. They degrade 21.88% of RB5 under UV-light illumination at the end of the process (180 min). The experimentally established results that the pure films are better catalysts compared to ZnO:Fe are in good agreement with the observed difference in the surface morphology for these samples (SEM images in Fig. 1).

The results confirm that the prepared films with significantly developed surface are better photocatalysts, as the higher surface area favors the rates of the heterogeneous photocatalytic reaction.

Decolorization of RB5 by ZnO films in darkness

The results from experiments without any illumination (Fig. 6) are compared with respect to the apparent rate constant *k*. The concentration of RB5 decreases also without illumination, but much slower in comparison with the respective photocatalytic counter parts. As seen from the data in Fig. 6, the rates of dye decolorization are very low for all the investigated samples. Among them highest degree of RB5 bleaching is achieved with the ZnO film – a trend, similar to the observed from photocatalytic experiments. This fact leads to the conclusion that the absorption stage plays significant role in photocatalytic reactions on ZnO surface. In case of experiments without illumination there is no crucial dependence of the rate constant *k* on the percent of the dopant, as well as on the initial dye concentration (C_0). As seen, linear fits for first-order kinetics are not much appropriate in this case. The decrease of RB5 concentration in these cases can be considered as the interplay of at least two processes: (i) adsorption of RB5 on the ZnO films surface and (ii) some kind of dye destruction process, taking part on the ZnO films even without illumination. This assumption needs further proofs and will be a subject of future studies. Despite these complications, we assume the simplification to fit the experimental data (from the experiments in darkness) as a single reaction process with rate constant *k* in order to compare this result to the results from the photocatalytic experiments.

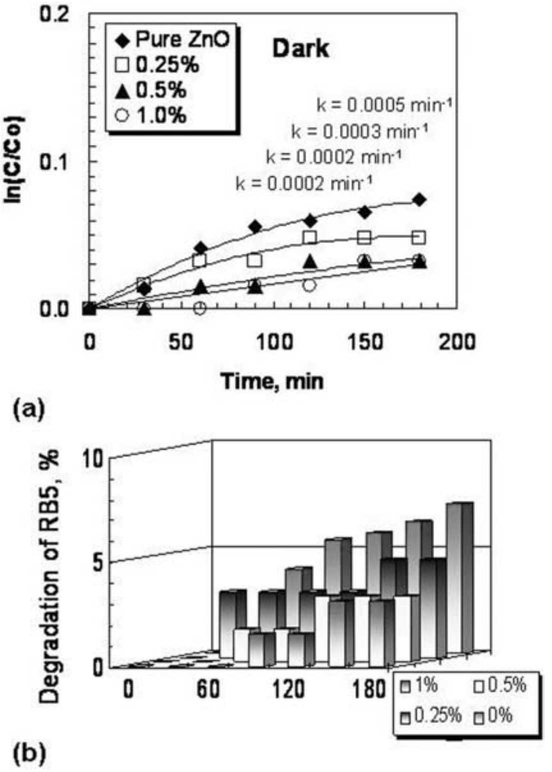

Fig. 6. Decrease of Reactive Black 5 by ZnO and ZnO-Fe films in darkness. The initial concentration was 3 ppm

CONCLUSIONS

Pure and iron doped ZnO films with two different coating configurations structure are deposited by sol–gel via dip coating technique. The films were characterized by SEM, AFM and UV-Vis spectroscopy. Nanostructured films manufactured by the first method demonstrate higher photocatalytic efficiency and faster mineralization of RB5 in comparison with these, prepared with the one of the second procedure. The addition of 0.25–1 wt.% of Fe^{3+} ions to the precursor modifies the film morphology (decreases the ganglia-like hills) and reduces the photocatalytic activity of ZnO. The kinetics of photocatalytic reaction is systematically studied under UV or visible light illumination and in darkness at different system parameters – amount of iron doping and the initial concentration of Reactive Black 5 in aqueous solution. The photocatalytic efficiency of pure ZnO films is higher than the activity, achieved by iron doped film under UV-light illumination, with a rate constant of 0.0153 min^{-1} (ZnO) much greater than that of 0.0013 min^{-1} (ZnO:Fe(1%)). The undoped films have the highest photocatalytic activity in comparison with the doped ones under visible light illumination. Our results are promising for the development of doped ZnO photocatalysts and their future application under visible light.

Acknowledgements: *This research is financially supported by FP7 project Beyond Everest and by the Erasmus Mundus External Co-operation Window Programme of the European Union (A.P.).*

REFERENCES

1. A. Fujishima, X. Zhang, D. Tryk, *Surface Science Reports*, **63**, 515 (2008).
2. A. Fujishima, X. Zhang, C. R. *Chimie*, **9**, 21 (2006).
3. A. Fujishima, X. Zhang, D. A. Tryk, *Internat. J. Hydrogen Energy*, **32**, 2664 (2007).
4. A. Ennaoui, M. Weber, R. Scheer, H. Lewerenz, *Sol. Energy Mater. Sol. Cells*, **54**, 277 (1998).
5. M. Vafaee, M. Ghamsari, *Mater. Lett.*, **61**, 3265 (2007).
6. Y. Kim, W. Tai, S. Shu, *Thin Solid Films*, **491**, 153 (2005).
7. Y. Wang, J. Li, P. Peng, T. Lu, L. Wang, *Appl. Surf. Sci.*, **254**, 5276 (2008).
8. T. Ohno, M. Akiyoshi, T.Umebayashi, K. Asai, T. Mitsui, M. Matsumura, *Appl. Catal. A*, **265**, 115 (2004).
9. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*, **293**, 269 (2001).
10. A. Eliyas, L. Dimitrov, V. Iliev, E. Stoyanova, S. Rakovsky, *Nanoscience and Nanotechnology*, Eds. E. Balabanova, I. Dragieva, BPS Publ. Co., **11**, 146 (2011).
11. A. Bojinova, C. Dushkin, *Reaction Kinetics, Mechanisms and Catalysis*, **103** (1), 239 (2011).
12. M. Uzunova-Buinova, D. Dimitrov, D. Radev, A. Bojinova, D. Todorovsky, *Mater. Chem. Phys.*, **110** (2–3), 291 (2008).
13. A. Eliyas, V. Iliev, I. Mitov, S. Rakovsky, *Nanoscience and Nanotechnology*, Eds. E. Balabanova, I. Dragieva, BPS Publ. Co., **10**, 38, (2010).
14. A. Shalaby, Y. Dimitriev, R. Iordanova, A. Bachvarova-Nedelcheva, Tz. Iliev, *J. Univ. Chem. Technology and Metallurgy*, **46** (2), 137 (2011).
15. R. Iordanova, A. Bachvarova-Nedelcheva, Y. Dimitriev, Tz. Iliev, *Bulg. Chem. Commun.*, **43** (3), 378 (2011).
16. A. Stoyanova, Y. Dimitriev, A. Shalaby, A. Bachvarova-Nedelcheva, R. Iordanova, M. Sredkova, *Journal of Optoelectronic and Biomedical Materials*, **3** (1), 24 (2011).
17. W. Zhang, Z. Liu, Z. Liu, J. Zhao, *Appl. Surf. Sci.*, **258**, 6103 (2012).
18. L. Xu, X. Li, *J. Cryst. Growth,* **312**, 851 (2010).
19. C. Wang, Z. Chen, Y. He, L. Li, D. Zhang, *Appl. Surf. Sci.*, **255**, 6881 (2009).
20. C. Ton-That, M. Foley, L. L. C. Lem, G. McCredie, M. R. Phillips, B. C .C. Cowie, *Mater. Lett.*, **64**, 386 (2010).
21. R. Saleh, S.P. Prakoso, A. Fishli, *J. Magnetism Magnetic Mater.*, **324**, 665 (2012).
22. A. K. Mishra, D. Das, *Mater. Sci. Eng. B*, **171**, 5 (2010).
23. M. L. Dinesha, H. S. Jayanna, S. Ashoka, G. T. Chandrappa, *J. Alloys Compd.*, **485**, 538 (2009).
24. F. Paraguay, D. M. Miki-Yoshida, J. Morales, J. Solis, W. L. Estrada, *Thin Solid Films*, **373**, 137 (2000).
25. G.-H. Kuo, H. Paul Wang, H. H. Hsu, J. Wang, Y. M. Chiu, C.-J. G. Jou, T. F. Hsu, F.-L. Chen, *J. Nanomat.*, **2009**, Article ID 316035 (3 pages) (2009) doi:10.1155/2009/316035.
26. A. Yu, J. Qian, H. Pan, Y. Cui, M. Xu, L. Tu, Q. Chai, X. Zhou, *Sens. Actuators B*, **158**, 9 (2011).
27. N. Han, L. Chai, Q. Wang, Y. Tian, P. Deng, Y. Chen, *Sens. Actuators B*, **147**, 525 (2010).
28. Q. Xiao, C. Yao, *Mater. Chem. Phys.*, **130**, 5 (2011).
29. S. Dong , K. Xu, J. Liu, H. Cui, *Physica B*, **406**, 3609 (2011).
30. H. Park, W. Choi, *Journal of Photochemistry and Photobiology A: Chemistry*, **159**, 241 (2003).
31. Gwyddion - data analysis software:///gwyddion.net.
32. T. Vicsek, Fractal Growth Phenomena, *World Scientific*, Singapore, 1992.
33. L. Znaidi, *Materials Science and Engineering B*, **174**, 18 (2010).
34. J. H. Sinfelt, *Surface Science*, **500**, 923 (2002).

ПОВЪРХНОСТНИ И ФОТОКАТАЛИТИЧНИ СВОЙСТВА НА ДОТИРАНИ С ЖЕЛЯЗО НАНОСТРУКТУРИРАНИ ТЪНКИ ФИЛМИ ОТ ZnO

Н. Кънева[1], А. Пономарева[2], Л. Кръстева[1], Д. Димитров[1], А. Божинова[1]*,
К. Папазова[1], Г. Сучанек[2], В. Мошников[3,4]

[1] Лаборатория по наука и технология на наночастици, катедра Обща и неорганична химия,
Факултет по химия и фармация, Софийски университет, София 1164, България
[2] Лаборатория по електроника на твърдото състояние, ТУ Дрезден, Дрезден 01062, Германия
[3] Катедра „Микро-наноелектроника“, Държавен университет по електротехника,
Санкт Петербург , 197376, Русия
[4] Катедра „Интегрирана електроника“, Санкт Петербург, Държавен политехнически
университет, Санкт Петербург, 195251, Русия

Постъпила февруари, 2013 г.; приета май, 2013 г.

(Резюме)

В настоящата работа изследваме наноразмерни Fe-ZnO тънки филми, отложени върху стъклени подложки чрез зол-гел метод и техника на потапяне на подложката (dip-coating). Прекурсорният зол е получен чрез разтваряне на $Zn(CH_3COO)_2.2H_2O$ и $Fe(NO_3)_3.9H_2O$ в 2-метоксиетанол, с добавка от моноетаноламин като повърхностно активен агент. Съдържанието на желязо в ZnO тънки филми е 0.25, 0.5 или 1 мас.%. Тънките наноструктурирани филми са с две различни покрития за фотокаталитичните тестове. Първите са получени чрез отлагане на 5 слоя от дотиран с желязо зол върху стандартни микроскопски стъкла. Вторият тип йерархично структурирани филми се отлагат върху стъклени подложки чрез двуетапна процедура. Фотокаталитичната ефективност на получените филми е тествана върху текстилно багрило, Реактивно Черно 5 (RB5) във воден разтвор при различни начални концентрации на багрилото, при облъчване с УВ или видима светлина. Изследвана е зависимостта на фотокаталитичната активност спрямо (i) съдържанието на желязо, (ii) наличието или отсъствието на ZnO подслой под Fe дотирания слой, (iii) честотата на облъчване и (iv) началната концентрация на багрилото. За обяснение на наблюдаваните резултати са извършени цялостни АФМ изследвания включително и фрактален анализ на повърхността (топография). Обсъдена е връзката между наблюдаваното фотокаталитично поведение на филмите и получените АФМ повърхностни характеристики.